

# Picosecond resolved XAS of photochemical transients

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## INTRODUCTION

Time-resolved x-ray absorption spectroscopy (XAS) is an emerging technique to study the electronic and geometric structures of photoinduced transient species. Herefore the usual pump-probe technique is employed, where an ultrashort laser pulse initiates the reaction and a time-delayed x-ray pulse probes the evolving electronic structure in the near-edge region (via XANES) and the atomic displacements (via EXAFS). XAS is undertaken at energies in the vicinity of the core electron excitation of an inner-shell electron, and is thus element specific. It requires no periodic structures and therefore is an ideal tool to study disordered and other complex systems. We have recently developed an experimental setup at beamline 5.3.1 of the Advanced Light Source (ALS) to study prototype photochemical reactions of solvated organometallic molecules [1,2]. We have pushed the sensitivity of our setup to the shot-noise limit of the pulsed x-ray source in order to use only single x-ray pulses in a pump-probe scheme (with a 1 kHz exciting fs laser). While we have maintained convenient total data accumulation times in the 10 min range (or ca. 1 sec per data point) we have boosted the temporal resolution for time-resolved XAS into the sub-100 ps range.

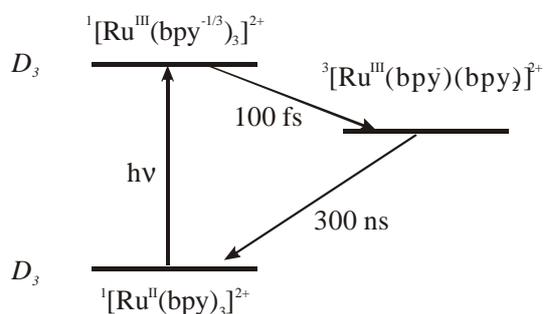
## EXPERIMENTAL SETUP

The ALS *camshaft mode* consists of a close-packed multibunch train followed by a 100 ns empty section, in which a ten-fold denser single electron bunch is placed. We single out its x-radiation at beamline 5.3.1 (detected with a fast APD behind the sample) with a gated integrator (opening window ca. 10 ns). In order to record high-quality spectra in a pump-probe configuration we have employed the following scheme: The gated integrator is triggered at twice the laser repetition rate, so that every second x-ray pulse corresponds to the static (= unexcited) sample, while the other x-ray pulses monitor the transmission following photoexcitation at the chosen time delay. Therefore, the gated integrator delivers an output of alternatively laser-pumped and unpumped intensities, which are then read into the computer and appropriately sorted. With this scheme we record high-quality XAS spectra of the photoinduced changes by subtracting the laser-excited from the dark spectra. Indeed, a careful analysis of the measured noise shows that we have nearly achieved the shot noise limit in this configuration. After correcting the statistically derived effective flux for the limited x-ray absorption in the 30  $\mu\text{m}$  thick APD, our measurements are very close to the specified flux of this beamline [2].

## RESULTS AND DISCUSSION

With our setup to record transient x-ray absorption spectra of photoexcited intermediate compounds we have investigated the photoexcited metal-to-ligand charge transfer triplet state <sup>3</sup>(MLCT) of aqueous tris-(2,2'-bipyridine) ruthenium (II),  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ . The photoexcitation cycle

(which is completed on a sub-microsecond time scale) is displayed in Fig. 1. This reaction involves a change of oxidation state of the Ru central atom, which can be probed by X-ray absorption using XANES around the ruthenium  $L_3$ -edge.



**Figure 1.** Photoexcitation cycle of the solvated reactant species in its singlet ground state leads to formation of an intermediate triplet excited state of  $[\text{Ru}^{\text{III}}(\text{bpy})(\text{bpy})_2]^{2+}$ , which radiatively returns to the initial reactant state after ca. 300 ns.

**Figure 2:** X-ray absorption near edge structures (XANES) of the investigated complex. a) Static  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  measured under pump-probe conditions at beamline 5.3.1 (black curve R) together with the constructed product state absorption spectrum (red curve P). b) Transient absorption spectrum T after 60 ps of laser-excited  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  together with a fit (red curve).

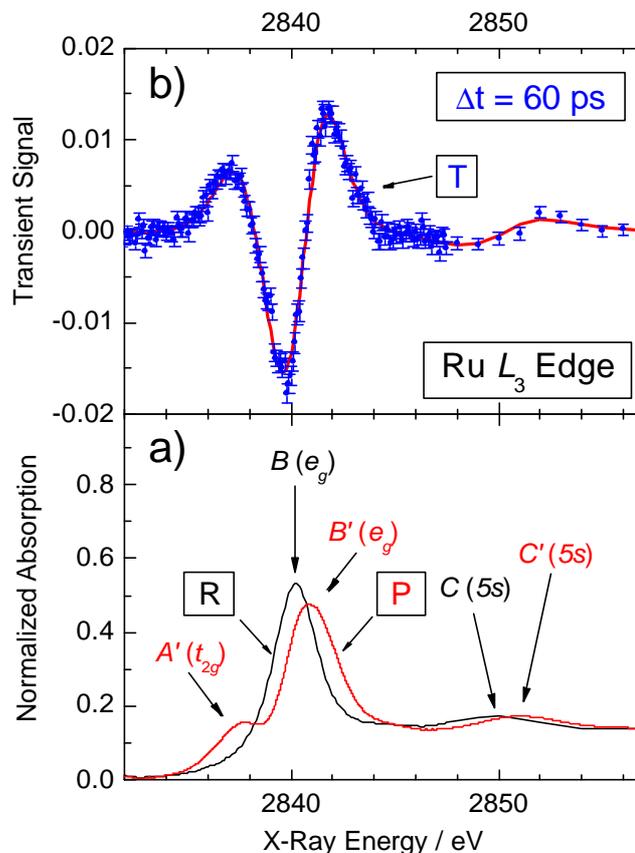


Fig. 2a displays our static XAS measurement under real pump-probe conditions (i.e., before laser excitation, curve R) of aqueous  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ . Feature B is due to the  $2p_{3/2} \rightarrow 4d(e_g)$  absorption, C due to the  $2p_{3/2} \rightarrow 5s_{1/2}$  transition [3]. Fig. 2b shows the transient absorption spectrum between the dark and the photoexcited sample after 60 ps. We can thus construct the product state absorption spectrum (curve P in Fig. 2a) from the transient spectrum (T) using the reactant state spectrum (R). The transient spectrum thus contains the expected energy shift due to the increased oxidation state of the central Ru ion ( $B \rightarrow B'$  and  $C \rightarrow C'$  are both shifted by 1.2 eV), and the appearance of the now accessible  $2p_{3/2} \rightarrow 4d(t_{2g})$  transition (feature A'), since the pump laser photon removed an electron from the previously fully occupied  $4d(t_{2g})$  level into a  $p^*$  orbital of one of the bipyridine ligands. One of the fit parameters is the fraction of excited state species, and the value of 10 % is in perfect agreement with laser-optical measurements under comparable conditions (laser intensity, sample concentration and thickness) undertaken in the Lausanne laser lab.

The results presented here are indicative of a change in oxidation state of the central Ru atom after photoexcitation of the aqueous reactant according to the following reaction:



While this is in full agreement with the optical-only results [4], to date this measurement describes the first sub-nanosecond resolved x-ray absorption spectrum of a transient chemical species in

solution. Hereby we have successfully identified the excited state species in both x-ray absorption energy *and* in time. This result demonstrates the utility of current pulsed x-ray sources for future ultrafast XAS studies.

Particularly promising are the prospects of carrying out time-resolved structural studies via EXAFS. Indeed, the symmetry reduction from  $D_3$  to  $C_2$  has been deduced from femtosecond optical anisotropy experiments [4]. However, the modified transient structure of the  $^3(\text{MLCT})$  species has never been directly observed in experiment. Time-resolved EXAFS exploiting our new technique could permit us to measure the individual Ru-bpy distances of the intermediate species for the first time, provided that we have achieved the required sensitivity. With  $10^6$  photons per data point (corresponding roughly to one second accumulation time per data point in the 3-10 keV region at the bend magnet beamline 5.3.1 of the ALS), we have achieved a signal-to-noise ratio of ca. 20 (Fig. 2b) for measuring the 10 % amount of transient species via time-resolved XANES. Time-resolved EXAFS with this technique seems therefore feasible and future work will focus on exploiting this structural tool to study nuclear rearrangements with picosecond temporal resolution.

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